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CHARACTERIZATION OF NON-FERROUS SLAGS FROM CANADIAN SOURCES. PART I - HYDRATION OF CEMENTITIOUS MATERIALS WITH SPECIAL REFERENCE TO NON-FERROUS SLAGS.

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CHARACTERIZATION OF NON-FERROUS SLAGS FROM CANADIAN SOURCES. PART I - HYDRATION OF CEMENTITIOUS MATERIALS WITH SPECIAL REFERENCE TO NON-FERROUS SLAGS.

by

E. Douglas

SUMMARY

Byproducts of metallurgical processes such as non-ferrous slags are materials in which significant energy has been invested and lost through disposal. Blast furnace slags are currently used as cement replacements in concrete. Non-ferrous slags could be used to reduce costs in cemented mine backfill operations and in low strength concrete.

This report is concerned with the current state-of-the-art with respect to the cementitious properties of those classes of slags produced in quantity in Canada. The purpose of this report is to provide information upon which future research on Canadian non-ferrous slags can be developed.

CARACTÉRISATION DES LAITIERS NON-FERREUX D'ORIGINE CANADIENNE. PART I - HYDRATATION DES LIANTS CIMENTAIRES AVEC RÉFÉRENCE SPÉCIALE AUX LAITIERS NON-FERREUX

par

E. Douglas

RÉSUMÉ

Une quantité importante d'énergie est investie dans les sous-produits de processus métallurgiques, tels que les laitiers non-ferreux. Cette energie est perdue lorsque ces matériaux ne sont pas utilisés et s'accumulent dans les chantiers de dépôts. Les laitiers ferreux s'utilisent actuellement comme agent de substitution partiel avec le ciment dans la fabrication du béton. Les laitiers non-ferreux pourraient être utilisés pour réduire les coûts de remblai dans les opérations minières ainsi que le coût de la production du béton à faible résistance.

Ce rapport traite de l'état actuel des connaissances sur les propriétés liantes des laitiers non-ferreux, qui sont produits en quantités appréciables au Canada. L'objet de cet exposé est de fournir des éléments qui pourront permettre de développer un programme de recherche sur les laitiers non-ferreux d'origine canadienne.

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LIST OF SYMBOLS

C = CaO

S = SiO_2

H = H_2O

A = Al_2O_3

F = Fe_2O_3

SEM = scanning electron microscopy

w/c = water to cement ratio

DTA = differential thermal analysis

Δ G = Gibbs free energy change

INTRODUCTION

Slags from the pyrometallurgical recovery of copper, nickel and lead are produced in Canada in quantities that warrant their consideration as cementing materials. It has been established that approximately 3.7 million tonnes of copper, nickel and lead slags are produced each year by the Canadian metals refining industry. This compares with 16×10^6 metric tonnes potential capacity and 8.1×10^6 metric tonnes actual production of portland cement in Canada in 1982.

While the technology of utilization of iron blast furnace slags as cementing materials is well established in Europe and elsewhere in the world, the application of non-ferrous slags as cementing materials is not well established in concrete technology. Currently, some 200 000 tonnes per year of blast furnace slags are pelletized in Canada, about one half of which is ground for use in concrete as a supplementary cementing material. As for non-ferrous slags, although the possibility of their industrial application has not been fully explored, copper, nickel and lead slags have been evaluated for performance as cement components in mine backfilling materials. A Canadian patent has been granted on the use of copper slags with portland cement for such purposes.

This report addresses a number of fundamental issues related to the development of cementitious properties in non-ferrous slags. It is suggested that in spite of the chemical differences between portland cement and slags, the products of hydration in the presence of $Ca(OH)_2$ are sufficiently similar that they may be considered in a unified manner. The key factor in the chemistry of these materials is their ability to produce gel-like calcium silicate hydrates (C-S-H) on reaction with water. The main chemical differences are that portland cement contains sufficient CaO that the requirement for Ca^{2+} to produce significant amounts of C-S-H is met internally whereas slags and pozzolans require provision of an external source of Ca^{2+}.

Physically, the reactive components of portland cement are largely crystalline, anhydrous silicates, aluminates and alumino-ferrites. In this respect reactive slags and pozzolans differ in that they are reactive only when they are in a largely non-crystalline state which is achieved by quenching. The rates of hydration of portland cement, slag and pozzolans (and the individual components that are present in each of them) differ

markedly. This results in different rates of development of the products of hydration which in turn causes considerable differences in the morphology of the resulting hydrated cement pastes. In recent publications it has become clear that these morphological differences are associated with differences in pore size distributions and pore structure properties. These factors are probably responsible for the improved durability imparted to concrete by the use of slags and pozzolans.

The phenomenological nature with regard to the performances of blast furnace slags and blast furnace slag cements in concrete has been reported in technical literature. On the contrary, the state of knowledge with respect to non-ferrous slags is in the initial stage. Studies are required to establish the optimum properties of these materials and the performance limits to which they can be developed. Limited research on non-ferrous slags has been reported in the literature and a major research effort in this direction is required to explain the mechanism of the hydration reactions of non-ferrous slags and the effect of added activators, to utilize their full potential as binder materials in concrete.

Published data indicate that slags from Canadian metals refining industries could be used as supplements for portland cement in conventional concrete, mine backfill or controlled density fill applications. More extensive knowledge of the nature and properties of non-ferrous slags could greatly stimulate their application as cement supplements, particularly in mine backfilling applications in regions of Canada to which the transportation of portland cement is costly.

THE NATURE OF HYDRAULIC ACTIVITY

The development of strength by hydraulic materials is a complex process controlled by chemical, physical, mineralogical and kinetic factors.

This section of the report is concerned with establishing a general perspective of hydraulic activity as a background to more detailed considerations of the cementing action of non-ferrous slags.

CHEMICAL COMPOSITION AND THE MECHANISM OF THE HYDRATION REACTIONS AT ORDINARY TEMPERATURE

Chemically, inorganic cementing materials derive from the multi-component system:

$$CaO - MgO - SiO_2 - Al_2O_3 - Fe_2O_3 - SO_3$$

Portland cement, natural pozzolans, most fly ashes and many blast furnace slags may generally be considered on a simplified ternary system Ca - SiO_2 - Al_2O_3 with minor MgO, SO_3 and Fe_2O_3 (Fig 1a). Steel slags and non-ferrous slags are better represented in the system CaO - SiO_2 - Fe_2O_3 where CaO represents the sum of CaO, MgO and Al_2O_3 (Fig. 1b). Approximately 70 to 75 wt % of a portland cement clinker is formed by tricalcium silicate (C_3S) and β-dicalcium silicate (β-C_2S) with small amounts of Al_2O_3 and MgO dissolved in them. The calcium silicates with the dissolved impurities constitute phases called alite and belite, respectively, which in portland cement clinkers are found as small crystals embedded in a mixed crystalline interstitial material composed of tricalcium aluminate (C_3A) and a solid solution of lime, alumina and ferric oxide of variable A/F ratio, (C_4AF), known as ferrite phase (2). In addition, small amounts of calcium sulphate, usually in the form of gypsum are added to portland cement clinker during the grinding operation for the purpose of controlling the initial hydration reactions of the cement.

Hydration of Portland Cement

Each of the phases present in a portland cement reacts with water at a different rate to form hydration products of different composition, crystallinity and mechanical properties (Fig. 2) (3). Although the search for a definite explanation of the mechanism of the hydration reactions is still in progress, it is generally agreed that the course of cement hydration proceeds in three stages (4):

(1) Initial hydration reactions, which primarily involve the hydration of some of the C_3A and subsequent reaction of the C_3A in the solution with the gypsum added to the clinker of Portland cement for control of setting (Fig. 3). This reaction results in the formation of

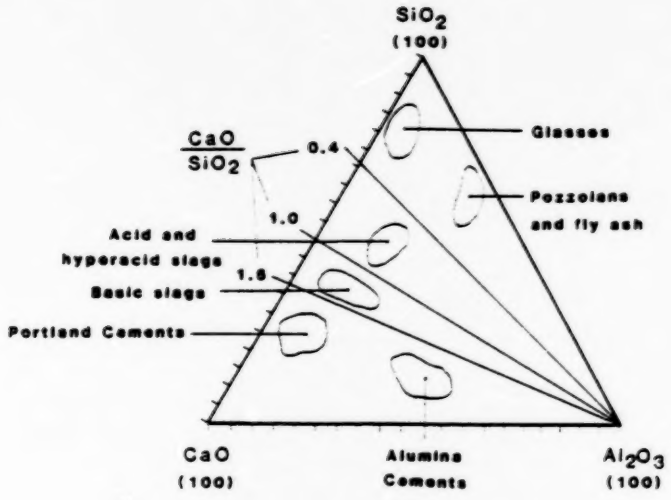

Figure 1a: Representation of some cementitious materials in the system $CaO - SiO_2 - Al_2O_3$

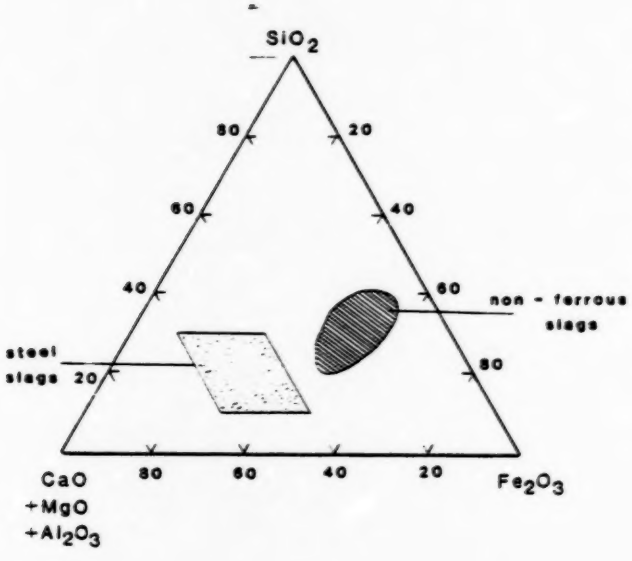

Figure 1b: Representation of some cementitious materials in the system $CaO - SiO_2 - Fe_2O_3$

either ettringite, monosulfate or calcium aluminate hydrate, depending on the amount of sulfate available to bind the C_3A in the solution (5,6,7). Approximately 1% of C_3S also reacts with water in the initial stage, releasing some $Ca(OH)_2$ (Fig. 3). Scant information on the factors affecting the extent of this reaction indicates that the chemical composition and the crystal structure of the alite phase as well as its degree of disorder are relevant to the initial hydration reactions (4). Small quantities of C_2S and C_4AF also react with water in the first 15 minutes after mixing, during which time the setting of Portland cement takes place. The hydration of the ferrite phase is similar, although slower, to that of C_3A (Fig. 2), the reactivity increasing with increasing A/F ratio (7,8).

2) A dormant or induction period, which lasts a few hours under normal temperature conditions. Two different conceptions lead to the explanation of the induction period by different reaction mechanisms (9). One theory postulates a halt of the chemical reactions, probably due to one of the following mechanisms: a) the blocking of the surface reactions of the cement constituents by the increasing concentration of various ions in the solution and subsequent nucleation of the $Ca(OH)_2$, which marks the end of the induction period (10); b) the development of a semipermeable membrane of hydration products (11,12); or c) the presence of a less reactive surface layer, richer in SiO_2, formed upon the dissolving of Ca^{2+} (13,14). Contrary to Young et al. findings (10), Fierens and Verhaegen (15,16), through thermoluminiscence, conduction calorimetry and Ca^{2+} concentration measurements, concluded that the induction period is not due to a protective layer but rather to a potential barrier corresponding to the critical size of the C-S-H nuclei (Fig. 4) (15,16).

The second theory is based on a continuous hydration process where the kinetics of the reactions is regulated by the evolution of the hydration products. The O^{2-} and SiO_4^{4-} ions at the solid-liquid interface go into solution upon hydroxylation. In the pore solution, the local Ca^{2+}, OH^- and SiO_4^{4-} concentrations result from their congruent solubility, their diffusion and their precipitation from oversaturated solutions. In this conception only the $Ca(OH)_2$ undergoes a dormant period since the hydration of the calcium silicate begins in the initial period but precipitates as calcium silicate hydrate (C-S-H), known as tobermorite gel, only when the pore solution is oversaturated with respect to the $Ca(OH)_2$ (17).

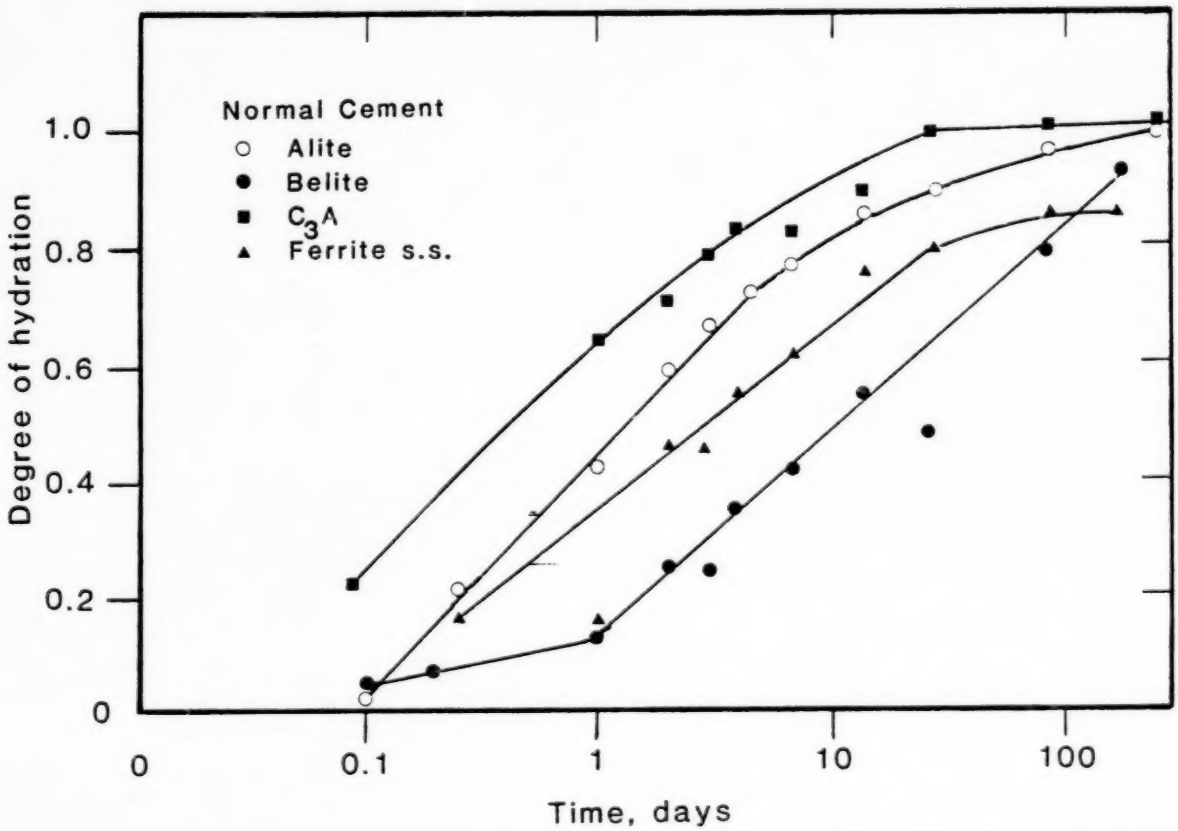

Fig. 2. Degree of hydration of a normal cement as a function of time (Ref. 3)

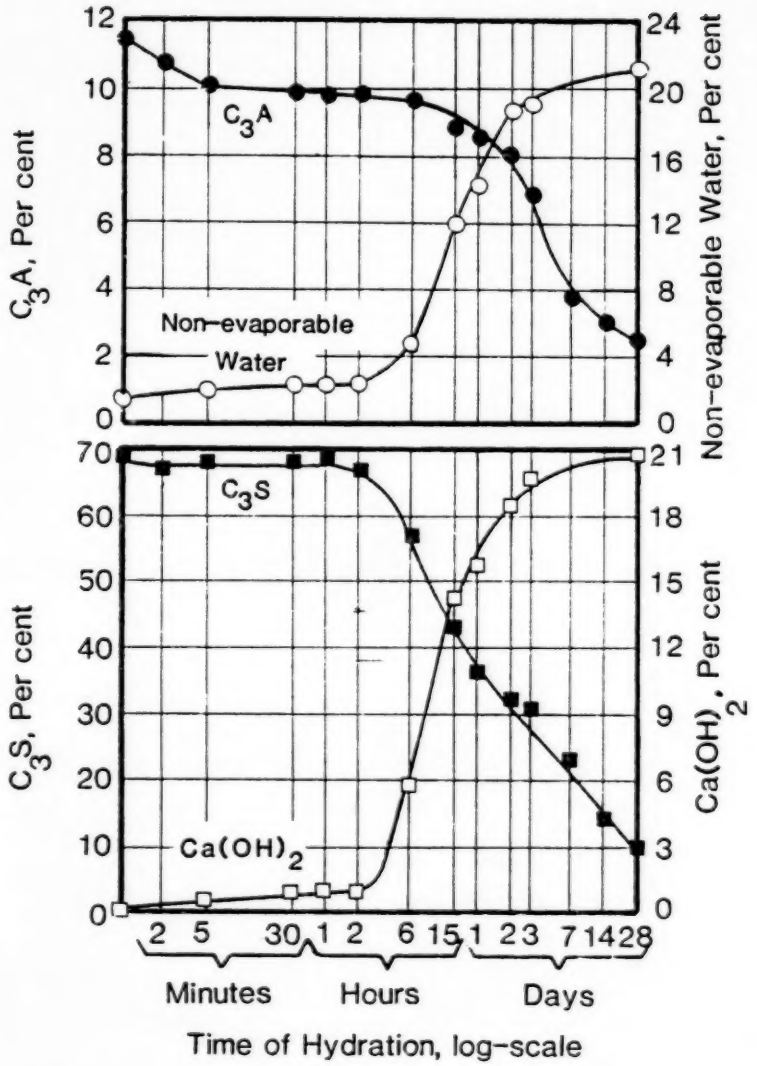

Fig. 3. Hydration of tricalcium aluminate and tricalcium silicate in Portland cement (Ref. 4)

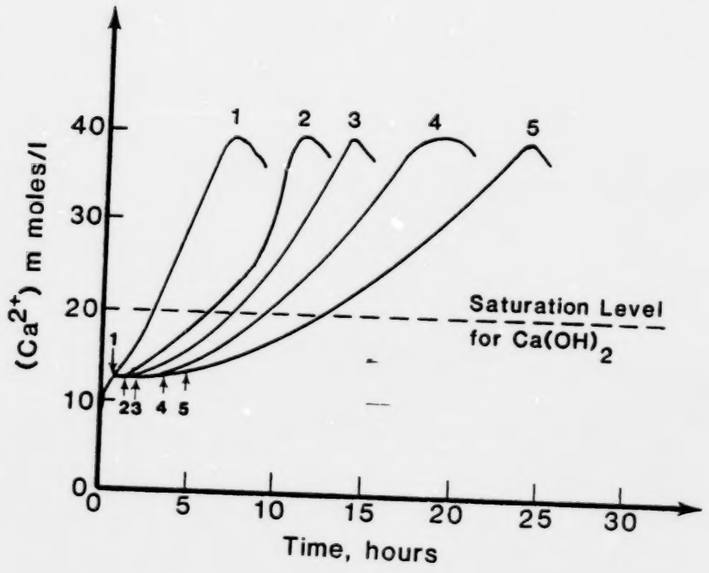

Fig. 4. Variation of Ca^{2+} concentration with time for five different samples of C_3S. Arrows indicate the end of the induction period, determined by conduction calorimetry (Ref. 13)

3) A hardening or acceleration period, where hydration of the calcium silicates occur and strength develops due to the gradually filling by the C-S-H of the pores formed in the initial period. This period of acceleration and diffusion controlled hydration has not been fully explained as yet due to the complexity of the set of reactions that take place and the lack of adequate instrumentation to establish the composition of the solid and liquid phases during the hydration process (18). It has been suggested that the acceleration period results from the change of the semi-permeable membrane of C_3S hydrates with high C/S ratio, formed during the induction period, into a layer of hydrates with $C/S < 3$. The change would result as a consequence of the transfer of Ca atoms, not coordinated with the silicate tetrahedra, into the liquid phase from the surface of the alite crystals (19). Other investigators postulate that the acceleration period is due to the formation of hydrate nuclei which disrupt the adsorption equilibrium of the complexes formed during the induction period, thus controlling the rate of hydration. The location of the new nuclei formed could be either the bulk liquid phase, the surface of certain impurities or an adsorption film. The kinetics of crystallization would be a function of the location of the nuclei (20). Measurements of changes of the Ca^{2+} and SiO_4^{4-} concentrations in the bulk solution and electron microscopy observations have been used to support the theory of osmotic pressure mechanisms. Skalny and Young (21) have presented a comprehensive review of the literature on the mechanisms of hydration of pure components of portland cement clinker and of portland cement at normal temperature.

For pure C_3S, Pommersheim and Clifton (22) developed a mathematical model for prediction of rate and degree of hydration, amounts of combined water, $Ca(OH)_2$ and C-S-H formed and intergranular porosity as a function of time. In portland cement-water systems the mechanism of the acceleration period seems to be rather similar to that of pure C_3S. Nevertheless, the factors relevant to the interaction of the components of portland cement clinker during the hydration process and the effect of gypsum as well as other minor components on the hydration and properties of cement pastes remain unanswered. Extensive research work is being continued in that direction (23,24,25,26,27).

Hydration of Pozzolan and Pozzoland Blends

It might be expected that materials as diverse as portland cement, pozzolans, and ferrous and non-ferrous slags would react with water to form markedly different compounds. In practice, there is a remarkable similarity in the reaction products from these materials. The common factor in all of these systems is the ultimate formation of C-S-H and the correspondence between its formation and the development of structural bonds in the hydrating mass.

Natural pozzolans of volcanic origin are composed of a vitreous phase of micro-porous texture with small amounts of crystalline phases (28). The silica and alumina, constituting the vitreous pyroclastic component, combine with lime in aqueous media yielding insoluble products with cementing properties. The reactivity of pozzolans is determined not only by the structure, morphology and chemical composition of the vitreous phase but also by the fineness of the material (29), type and quantity of lime added (30,31) and water content (32). Different hydration products have been identified on various pozzolan - $Ca(OH)_2$ systems. In some cases C-S-H together with C_2ASH_8 or C-S-H, C_2ASH_8, hydrogarnet and ($C_3A.CaCO_3H_{12}$ - C_4AH_{13}) were found depending on the composition of the pozzolan. The CaO/SiO_2 ratio in the C-S-H is believed to be closely related to the concentration of Ca^{2+} in the solution (33).

The results of studies on pozzolan-$Ca(OH)_2$ systems support the theory of the dissociation of the SiOH group on the surface of the grains at pH $>$ 12.6 which is maintained by the saturated $Ca(OH)_2$ solution. The dissociation of the SiOH group to SiO_4^{4-} and H^+ originates a negatively charged surface in which Ca^{2+} is adsorbed while the alkalies in the pozzolans are transfered to the liquid phase. The amorphous Si-Al layer on the grain surface combine with Ca^{2+} through dissolution, forming a layer through which SiO_4^{4-} and AlO_2^- diffuse at different velocities. Due to the differential diffusion rates, the concentration of ions inside the layer increases causing expansion as well as osmotic pressure build-up resulting in rupture of the layer. Hydrates of Ca-Al precipitate away from the grain surface due to the higher concentration of Ca^{2+} in the bulk solution while C-S-H is formed close to the pozzolan grains (33).

Similar mechanisms have been proposed on the hydration of pozzolan-C_3S and pozzolan-C_3A systems (34,35). These mechanisms are schematically shown is Figures 5 and 6. The hydration products in pozzolan - cement

blends seem to be of the same nature as those found in pozzolan - $Ca(OH)_2$ and pozzolan - cement compounds binders. Takemoto and Uchikawa have found ettringite, a solid solution of monosulfate hydrate - C_4AH_{13} and $Ca(OH)_2$ in the early stage of hydration while C-S-H was detectable only after 28 days (36).

Hydration Mechanism of Blast Furnace Slag and Slag Blends

Most ground granulated blast furnace slags, on their own, show little hydraulic activity. On contact with water, the CaS releases $Ca(OH)_2$ into solution which concentration could amount to 0.06 to 0.08 g/L after a few months with no detectable hydrated compounds in the slag (37). By contrast, the concentration of $Ca(OH)_2$ in a portland cement paste is approximately 16% after 24 hours hydration (Fig. 3), while hydration products are observed on the C_3S surface in the first 20 minutes (38,39). Some blast-furnace slags are nevertheless capable of hydraulic activity without addition of lime-bearing products, developing relatively low strength. These have been termed cementitious hydraulic slags.

The low hydration rate of the granulated blast furnace slag has been ascribed to the formation of acidic surface films as a result of the Ca^{2+} ions being released into the solution (40). More recent research work done on the hydration of blast furnace slag gives evidence of the presence of unidentifiable products of hydration after 2 to 4 days with increased concentration of Ca^{2+} and OH^- ions in the solution (41). The increasing ion concentration was attributed to the hydrolysis of the CaS present in the slag, producing $Ca(OH)_2$ and therefore activating the hydration process. Voinovitch et al. (42) emphasized the role of water in blast furnace slag hydration as a dissolvent of the slag components, which action is modified by an increase of the pH of the solution and subsequent release of Al into the solution. Recent studies on synthetic glasses of similar composition to the granulated blast furnace slag have led to the conclusion that, while portland cement clinker dissolves by hydrolysis, slags dissolve with intervention of OH^-, the process being pH dependent and notable only at $pH > 12$ (43). According to Dron, the mechanism proposed by Le Chatelier for gypsum and cement can also explain the hydration reactions in slag-water systems: the dissolution of the slag components in contact with the solution result in a super-saturated solution of hydrates which in turn crystallize, bringing the solution

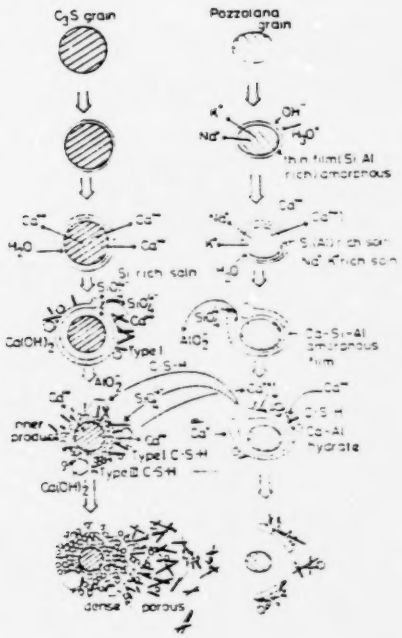

Fig. 5 - Schematic explanation of the mechanism of hydration in the system pozzolan-C_3S (Ref. 34)

Fig. 6 - Schematic explanation of the mechanism of hydration in the system pozzolana-C_3A in the presence of $Ca(OH)_2$ and $CaSO_4.2H_2O$ (Ref. 35)

close to saturation and therefore establishing a dynamic equilibrium between dissolution and crystallization. In the case of slag hydration, where the hydration products have the same crystallization rate as those of cement, the kinetics of the hydration reactions is governed by the low solubility rate. Dron's study shows that, for synthetic glasses in $CS-C_2AS$ series the dissolution rate is a linear function of the ionic fraction of Al, x = Al/Al+Si, suggesting that the reactivity of a slag is due to the presence of the coordinated Al in the macroionic network that constitutes the glass. The initial reaction would be determined by the presence of the OH^- ions reacting with the Al arranged in a fourfold configuration corresponding to the monoaluminates (Fig. 7). The initial reaction results in the regeneration of the OH^- and a change of the Al coordination to that corresponding to a bi-calcium aluminate, configuration Y. In those conditions, further hydration takes place by hydrolysis and Si and Ca ions are released into the solution.

Based on studies done on the dissolution rates of the elements Ca, Al and Si in a NaOH solution of pH = 12.6, Dron and Brivot (44) proposed to characterize the reactivity of blast furnace slags by determining the concentrations of the elements in solution.

Effect of Activators

For the majority of blast furnace slags, including cementitious slags, activators are required if significant hydration is to occur. The activators used in modern practice are portland cement or mixtures of portland cement and calcium sulphate. Other activators include sodium and potassium hydroxides or other compounds which yield highly alkaline aqueous solutions. For practical purposes, activators are usually limited to portland cement, calcium hydroxide, calcium sulphate or combinations of these materials.

The studies on synthetic glasses of similar composition to those found in granulated blast furnace slags (37) show a gradual decrease in the concentration of $Ca(OH)_2$ and eventual halt of the hydration reaction in blast furnace slags suspended in initially saturated $Ca(OH)_2$ solutions. Continuation of the slag hydration reaction is only possible when the concentration of $Ca(OH)_2$ is maintained at saturation levels. Recent theories (43) explain the activating effect of $Ca(OH)_2$ and NaOH in terms of hydroxylic attack of the slag components of pH 12.

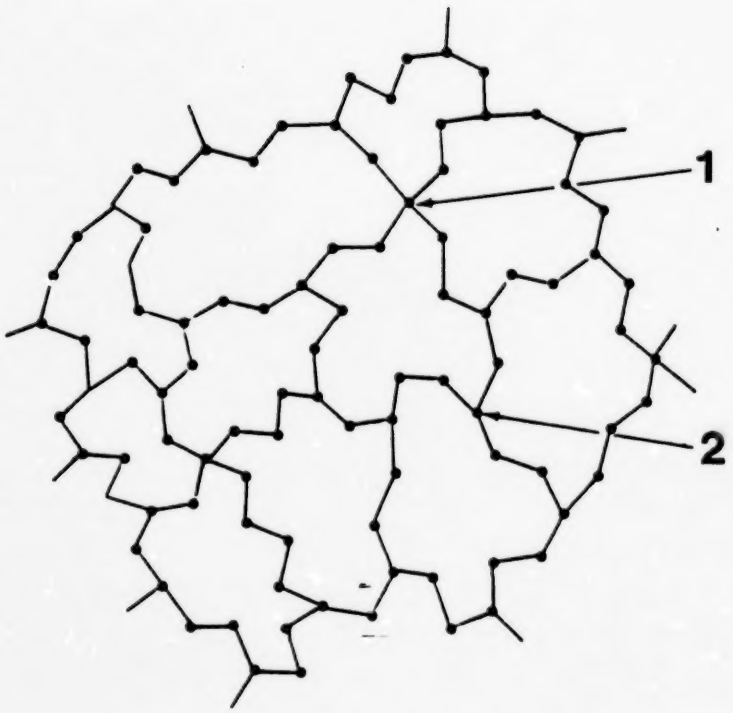

Fig. 7 - Schematic structure of the macroionic network.

1. Al in fourfold coordination or X configuration
2. Al in Y configuration (Ref 43)

In the case of alkaline activation with NaOH the hydration products are C-S-H, C_4AH_{13} and C_2ASH_8. Lime activation yields C-S-H and C_4AH_{13}. Scanning Electron Microscopy (SEM) studies on pastes have shown that the Al hydrates play the role of crystalline bridges between the slag grains (45). A hydrate of ratio C/S+A ≈ 2.7 at the early stage of hydration and approximately 1.7 at 180 days was found in slag/lime pastes of w/c = 0.20 (46). Fierens and Poswick (47) studied the hydration, using 1M NaOH solution instead of water, of industrial blast furnace slags quenched at different temperatures and media. It was shown that the kinetics of the hydration reactions depend in great extent on structure defects of the glass phase, formed under different quenching conditions.

Sulphate activation in the absence of calcium ions results in the formation of C-S-H, ettringite and $Al(OH)_3$. Hydration takes place very slowly in pastes of w/c = 0.5 with no strength development at 28 days, at which time unreacted gypsum has been detected by X-ray diffraction (45). The $Al(OH)_3$ combines with the gypsum as ettringite when the pH is modified by the presence of NaOH or $Ca(OH)_2$. In this case, half of the gypsum is consumed after the second day. A combined lime-sulphate activation takes place during the hydration of blast furnace slag cements. Slag-rich cement pastes made of equal weights of slag and clinker ground to the same fineness were prepared with a w/c = 0.20 (48). The results of the hydration kinetics studies led to the belief that during the early stages the $Ca(OH)_2$ released in the hydration of clinker activates the hydration of the slag, the rate of hydration being related to the porosity of the paste. In the final stages of hydration, which is diffusion controlled, the free lime content increases, indicating a much slower rate of hydration of the slag as compared with that of the portland cement clinker. This study confirms the results reported by de Jong (41), i.e., the acidic surface film formed by alkaline activation at the initial stage reacts with SO_4^{2-} ions resulting in a more permeable layer of basic silicate hydrate which is formed when a critical concentration of $Ca(OH)_2$ in the solution is reached. At the same time higher $Ca(OH)_2$, concentration increases the pH and stop or delay further sulphate activation. Subsequently, $Ca(OH)_2$ originated in the hydration of the alite phase of the portland cement clinker contributes to the formation of

C-S-H which precipitates on the surface of the slag, retarding again further hydration of the slag grains. At this point diffusion reactions take place resulting in a continuous removal of the Ca^{2+} ions due to the formation of insoluble hydration products. Regourd et al. (45) found that the ettringite crystallized in the initial stage of hydration evolved into monosulfoaluminate and finally formed a solid solution with C_3A. The C/S ratio in the hydration products range from 1.5 to 2.0 while the C/S in blast furnace slags is approximately 1.2 to 1.3 (41).

The effect of alkaline and sulphate activators has been also studied by Kondo et al. (49). The results of the study show that the weight per cent of hydrated products does not increase beyond the 5 per cent of $Ca(OH)_2$ produced in the hydration of the portland cement clinker. Using soda as activator the amount of hydrated products at 1 day seems to be a function of the weight per cent of NaOH added (Fig. 8). The same trend is observed for sulphate activation with gypsum but when combined with lime activation, as in supersulphate cements, there seems to be an optimum lime content for a maximum weight of hydration products formed, beyond which there is a decrease until an approximately constant value is reached at the three ages tested.

Voinovitch and Dron (50) have taken a different approach and have considered the four component system $CaO-SiO_2-Al_2O_3-H_2O$ in terms of Gibbs "Phase Rule" with respect to different activators. Figure 9 illustrates their conclusions for alkali and sulphate activation. In alkali activation the solid phases expected at equilibrium after hydration are represented by the hydrates indicated at the corners of triangles I through VI in Fig. 9a. The individual products are determined by the triangle containing the initial anhydrous compositions. These comprise such components as pozzolans, slags, portland cement, lime or their combination. For example, for anhydrous compositions A, B and C, the hydration products indicated in Fig. 9a would be expected.

Figure 9b shows the concept extended to activation in the presence of gypsum. This results in the delineation of three equilibrium regions (Ig, IIg and IIIg) and $Ca(OH)_2$, C-S-H, $Si(OH)_4$, $Al(OH)_3$ and attringite as the stable hydrates. Again, considering the three model compositions A, B and C, the products of gypsum activation are indicated in Fig. 9b.

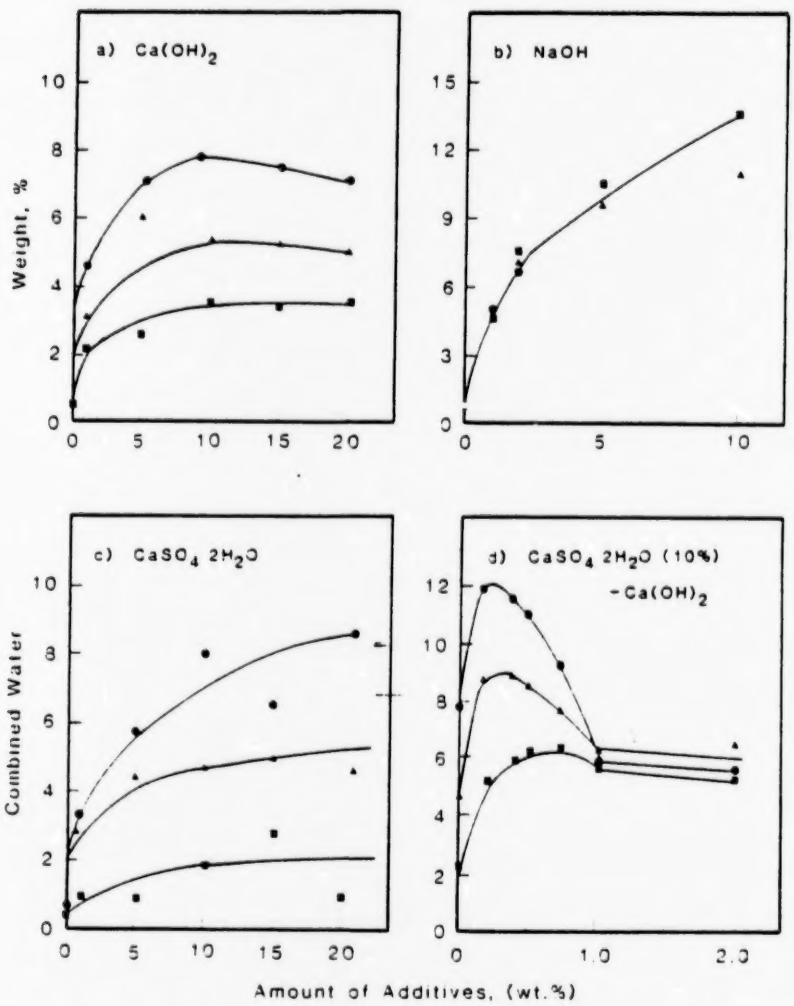

Fig. 8 - Amount of combined water during the hydration of granulated blast furnace slag with various activators (■ 1d, ▲ 3d, ● 7d) (Ref. 49)

Area	Lime/alkali activation	Type of system
I	$Al(OH)_3$, C-S-H, $Si(OH)_4$	Pozzolan
II	$Ca(OH)_2$, C-S-H, C_4AH_{13}	B.F. slag + lime
III	C_4AH_3, C-S-H, C_2ASH_8	B.F. slag + alkali

Area	Gypsum activation	Type of system
Ig	$Al(OH)_3$, C-S-H, $Si(OH)_4$	Pozzolan
IIg	$Ca(OH)_2$, C-S-H, $C_3A\bar{S}_3H_{32}$	B.F. slag+gypsum
IIIg	$Al(OH)_3$, C-S-H, $C_3A\bar{S}_3H_{32}$	B.F. slag+portland cement

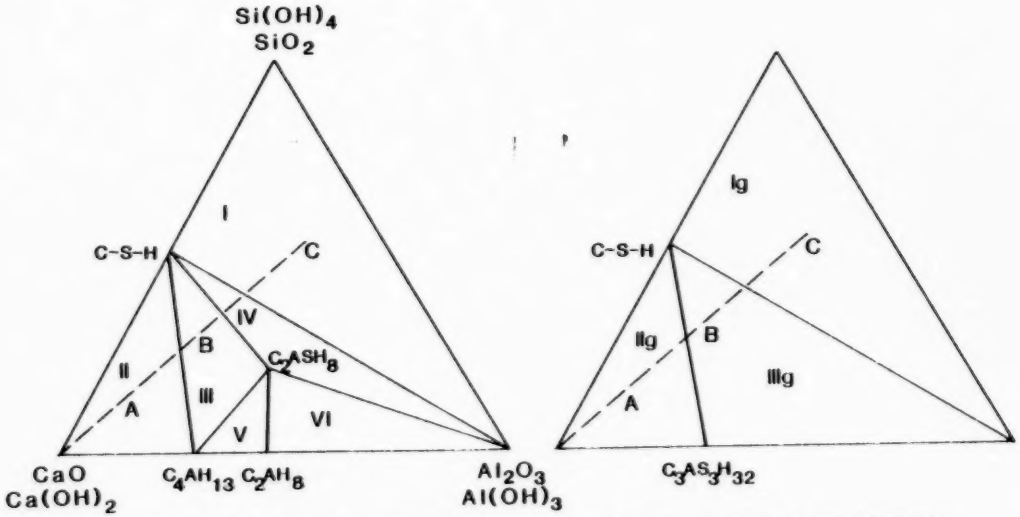

Fig. 9 - Idealized equilibrium fields of hydration products for cementitious systems in the presence of alkali or sulphate activators (Ref. 50)

Such an approach is limited by the very approximate nature of its assumptions, namely:

(a) that slags are ternary systems;

(b) that equilibrium is attainable in paste hydration;

(c) that C-S-H has a definite stoichiometric composition.

However, the approach is valuable in that it seeks to direct attention to certain phases as potential hydration products; to emphasize the role of C-S-H as a hydration product and to place the understanding of slag hydration on a thermodynamic basis.

Despite the limitations of this conception it indicates that from the chemical standpoint, slags are hydraulic, i.e., form C-S-H on hydration, as a result of chemical combinations with $Ca(OH)_2$ or gypsum rather than through catalysis or "activation" by $Ca(OH)_2$ as in the case of activation with NaOH.

From the viewpoint of hydration mechanisms of slag cements, two lines of thought point out in different directions. On one side are the followers of the dissolution - diffusion - precipitation theory, originally formulated by Le Chatelier (51) and supported by recent experimental evidence (45,52). According to this theory, blast furnace slag and portland cement clinker dissolve simultaneously at different rates until a chemical coupling effect takes place, reciprocally affecting the kinetics of hydration of both blend components. Opposing this theory, some investigators advocate the occurrence of topochemical reactions (48,49) between the slag grains and the $Ca(OH)_2$ in solution. Regourd (53) finds that a dissolution - diffusion - precipitation process takes place when the slag is activated with NaOH while a topochemical reaction that seems to occur in slags activated with gypsum is in fact a result of precipitation of C-S-H in strongly supersaturated solutions, close to the slag grain. No definite conclusions concerning hydration mechanisms in the presence of activators have been drawn as yet. Ultimately, studies on the structure of the vitreous slags as related to their hydraulic reactivity could contribute to a better understanding of the hydration reactions. In general terms, blast furnace slags are considered potentially hydraulic because they can provide SiO_2 and Al_2O_3 to a solution containing Ca^{2+} ions derived from either the slag itself, portland cement, lime or gypsum. On this basis the reactivity of blast furnace slag differs from that of portland cement in that the source of

Ca^{2+} is largely external to the slag. It differs from the reactivity of pozzolans in that the quantity of Ca^{2+} required is usually much less for blast furnace slags than for pozzolans. The effect of adding $Ca(OH)_2$ to blast furnace slag, or pozzolan, is to form an overall composition that chemically corresponds to a point within triangle II in Figure 9a. The inclusion of $CaSO_4$ modifies the system so that a composition in triangle IIg of Figure 9b is obtained.

Hydration of Non-ferrous Slags

The utilization of non-ferrous slags in the manufacture of hydraulic binders has been only known for the past 15 years. A German patent (54) described a product consisting of cement and 10% copper slag, ground to a specific surface of 3200 cm^2/g. Laboratory tests of a similar material were carried out in Australia (55). Binders containing up to 10 wt % ground reverberatory furnace slag(1) and 8 to 10 wt % lime as well as binders made of portland cement slag mixes were proportioned to test their performance as cemented hydraulic fill in mining operations (56). Thomas (57) showed that the pozzolanic behavior of copper reverberatory furnace slag, lead blast furnace slag and copper converter slag(2) was related to the degree of vitrification upon quenching and to the fineness at which the slags had been ground. Slags ground to around 3000 m^2/g, measured by the Blaine method, exhibited pozzolanic behavior. A Canadian patent (58) introduced a binder consisting of 70 to 55 parts by weight of portland cement and 30 to 45 parts of granulated nickel or copper slag, ground to a specific surface of 3800 cm^2/g, yielding 90-day to 1-year mortar strength values approaching those of portland cement mortars. The patent pointed out the two basic conditions already mentioned by Thomas (57) under which a copper or nickel slag could be used in hydraulic binders: a) vitreous state of the granulated slag and, b) fineness. Results of optical and SEM studies carried out in Spain (59) on granulated copper slags, showed that the crystalline phase was composed mainly by needle-like structure fayalite (Fe_2SiO_4) and globular iron oxides.

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(1) Copper concentrate and fluxes are melted to form a matte and an iron silicate slag.

(2) Slag produced in the converting operation, where iron sulphide is oxidized and the iron oxides combine with silica flux to form a slag.

Hydration products of pastes made with 25 wt % $Ca(OH)_2$ and 75 wt % granulated copper slag, with a w/c ratio of approximately 0.25, were studied by X-ray diffraction, differential thermal analysis (DTA) and SEM (59). Samples cured at room temperature showed 13% uncombined $Ca(OH)_2$ after 28 days and poorly crystallized C-S-H with alveolar and vermiculate structure. A natural pozzolan, cured in the same conditions, contained 11% uncombined $Ca(OH)_2$ after 28 days, C_4AH_{13} and the same type of C-S-H as in the copper slag paste. After 300 days, 4% of unreacted $Ca(OH)_2$ was detected in both, natural pozzolan and copper slag pastes. In addition C_4FH_x was detected in the slag paste.

More recently, studies on the effect of physical and chemical properties of copper reverberatory furnace slags on the reactions underlying strength development were carried out by Roper et al. (60). Data were presented on slags with an approximate glassy to crystalline phase ratio of 1:1. Zoned crystals of fayalite and crystals of magnetite, quartz and chromite were identified. The glassy phase was enriched in SiO_2, CaO, Al_2O_3 and SO_3. The heat of hydration, measured in slags ground to around 6 000 cm^2/g, evolved in the first 15 hours in slag-$Ca(OH)_2$ blends with a water to cement ratio of $\geq$0.40, showing maximum early heat evolution at a slag/$Ca(OH)_2$ ratio of approximately 4:1 (Fig. 10). A crystalline hydrate detected by X-ray diffraction presented a peak at 0.734 μm, with maximum intensity in pastes containing 90 wt % slag and 10 wt % $Ca(OH)_2$. In slag-portland cement pastes, the maximum intensity of the unidentified hydrate peak corresponds to a mix of approximately 75 wt % slag and 25 wt % cement.

Boldyrev et al. (61) explained the pozzolanic properties of non-ferrous slags as the result of their aptitude for an acid-base interaction with an aqueous solution of hydrated lime with formation of insoluble hydration products. According to their study an indication of the pozzolanic activity of a slag is given by the concentration of the $Ca(OH)_2$ in the liquid phase of the system, which should remain below the equilibrium concentration for a given temperature and pH.

Laneuville (62) studied the hardening of pastes of air-cooled and granulated nickel slags, the latter presumably with a higher content of glass. The results of the study indicated that the amount and nature of the hydration products in slag-cement pastes vary with the composition of the binders and the time of curing.

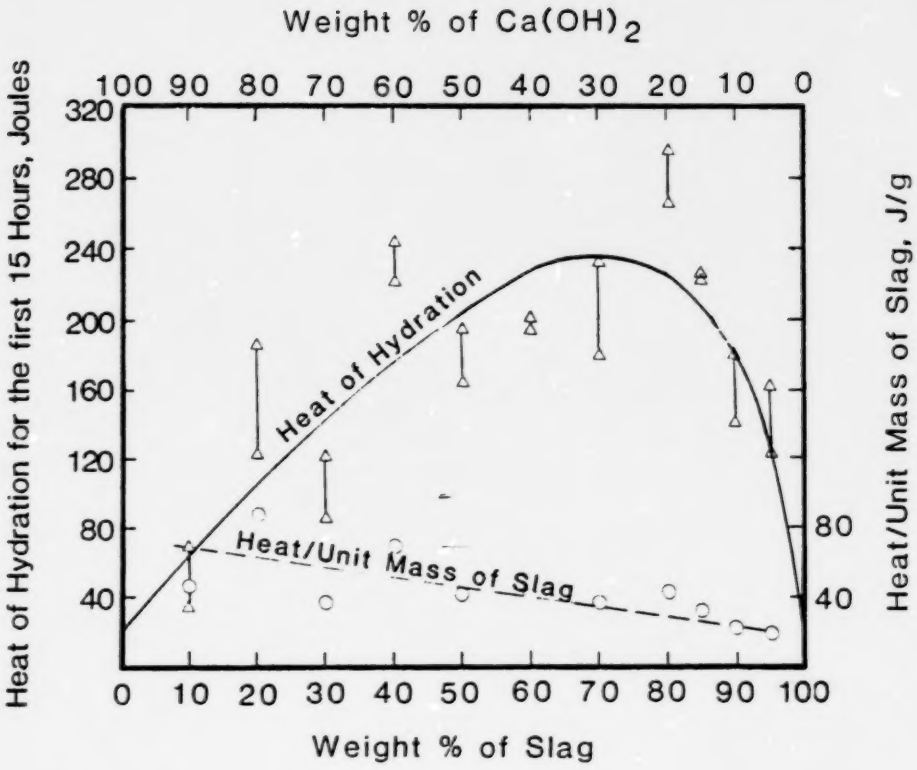

Fig. 10 - Relationship between heat of hydration and the percentage of slag in the mix (Ref. 60)

Granulated nickel-copper electric furnace slag was tested for its cementitious properties when used as partial replacement for portland cement in cemented tailings fill (63). The glass content, 95%, was measured by a X-ray diffraction method (64). Measurements of the chemically bound water in the hydrated slag-cement mix up to 56 days, performed at different curing times, indicated increasing hydration of the slag.

Other non-ferrous slags which were the subject of studies include a magnesium slag, rich in CaO (65). Hydration products of the powdered fraction, formed primarily by γ-C_2S, were C_2AH_8, CAH_{10} and CAH_{13}, detected within two hours after mixing with water. C_2ASH_8 appeared when the concentration of $Ca(OH)_2$ in the solution diminished, while C_3AH_6 was the last hydrate to be detected. The granulated fraction of the slag, constituted by crystals of α and β-C_2S embedded in a glass phase, did not produce hydrates in the first 24 hours after mixing with water. After that time mainly aluminates and hydrated gehlenite, C_2ASH_8, were detected. Mixes of the powdered and the granulated fractions behaved as an hydraulic binder without addition of activators.

The properties and applications of non-ferrous slags have been attracting the interest of investigators in the Soviet Union (66-71), in Poland (72-74) and in Japan (75). Most studies are concerned with the morphology, pore structure and strength development of non-ferrous slags binders. Much research needs to be done to understand the reaction kinetics of the individual components of the slag binders, underlying their physical and mechanical properties.

GLASS STRUCTURE AND HYDRATION OF SLAGS

A mineralogical examination of portland cement clinker reveals the presence of large euhedral crystals of C_3S and anhedral crystals of C_2S embedded in an alumino-ferrite interstitial matrix. Blast furnace slag, that has been satisfactorally granulated, comprises largely a vitreous mass, somewhat porous, with a few grains in interspersed melilite crystals (76). Pozzolans vary to include: amorphous hydrous silica such as opal, amorphous diatoms, amorphous or disordered expanded dehydrated clays and glassy fly ash. The principal difference between portland cements and slags or pozzolans is that in the spontaneously active portland cement the

rate of hydration of C_3S and C_3A in the crystalline state is very rapid, at least up to the point at which the cement grains are coated with hydration products. In slags and pozzolans, the crystalline phases are largely inert, the glassy and amorphous phases react with water but only relatively slowly.

The key to understanding the kinetics of slag hydraulicity lies in an understanding of the glass reactivity attributed mostly to its disordered physical state.

The most difficult decision in examining rapidly quenched materials is whether the designation "glass" should be used rather than a more broadly based designation such as "amorphous", "non-crystalline solid" or "short range ordered solid". It is not correct, as other authors in the field of slag chemistry have done, to use such terms interchangeably. This is not merely a matter of semantics, the behaviour of materials designated in each of these classes differs in ways that are critical to their detection and quantitative estimation. It is perhaps true to claim that much of the lack of progress to date in evaluating the function of molecular-order in determining the reactivity of slags has resulted from misconceptions about such terms as "amorphous", "non-crystalline" and "glassy".

ASTM (77) defined "glass" as "...an inorganic product of fusion which as been cooled to a ridged condition without crystallizing". This is a functional definition that essentially accounts for glasses as greatly supercooled liquids of extremely high viscosity (at ambient temperatures) that appear as solids.

Most materials melt to form liquids having a different viscosity. When the material in the liquid state is cooled, rearrangement of the component molecules (or ions) occurs and crystallization follows. Some crystallization still takes place even when cooling is rapid. However, a number of materials melt to form very viscous liquids (10^5 to 10^6 Pa.s at 500 to 1800°C). If such a liquid is held at a temperature just below its freezing point, it will slowly crystallize. If, instead, the liquid is rapidly cooled, crystallization may not occur. The viscosity of the liquid increases steadily as the temperature is reduced until eventually it is so high that the material is apparently solid. Such a material may be considered as being rapidly quenched, it is likely high disordered at the molecular level, although it is not necessarily a glass.

The importance of the physical state of quenched solids relates to their reactivity and can be summarized in terms of the free energy of reaction. Nassau, Wang and Grasso (78) have discussed the surface hydration of glasses in the (Li-Ca-K) NbO_3 - TaO_3 system in terms of free energy. Assume that a glass undergoes a transformation by which a crystalline material forms and that such material does not hydrate in the ambient atmosphere. If there are no kinetic barriers, the Gibbs free energy involved in the transformation will be negative, i.e., the process tends to proceed spontaneously:

$$\text{glass} \rightarrow \text{crystal}; \quad \Delta G_{g,c} = \text{negative}$$

For the crystal to hydrate, the Gibbs free energy will be positive and the process will tend to proceed spontaneously in the opposite direction:

$$\text{crystal} + H_2O \text{ ambient} \rightarrow \text{hydrate}; \quad G_{c,h} = \text{positive}$$

The subscripts g, c and h stand for glass, crystal and hydrate, respectively. When the glass hydrates at ambient temperature, the net free energy change will be:

$$\text{glass} + H_2O \text{ ambient} \rightarrow \text{hydrate}; \quad \Delta G_{g,h} = \Delta G_{g,c} + \Delta G_{c,h}$$

If the value of $\Delta G_{g,h}$ is negative, the glass will hydrate even if the crystal does not. With respect to slag reactivity, the fractions of material in either glass, non-crystalline solid or metastable crystalline state formed upon quenching must be taken into account. The Ostwald step rule may be expected to apply to metastable transitions between different states, where the solid phase produced is not the most stable under the existing conditions but the next in thermodynamic order. The net free-energy change, $\Delta G_{m,c}$, involved in the change from metastable to crystalline state, will determine the slag reactivity. The system reduces its free energy in a succession of steps, kinetically controlled and subject to the effects of diffusion and solid solubility. These changes are observed in the process of devitrification where uncontrolled formation of crystals in a glass during melting, fusion or secondary process takes place. The crystals grow homogeneously within the glass

or heterogeneously at the air-glass interface. A quenched slag is usually stored, dried, ground and exposed to a number of environmental changes before finally being mixed with cement or lime and water. Each stage of this process may induce changes between metastable states, each one reducing the value of $\Delta G_{m,c}$ and consequently reducing its potential reactivity. These changes might be the main source of uncertainty in the correlation of the physical properties of various slags from various sources with the development of cementitious bonds.

Blast furnace slags have a heat of crystallization of about 200 joules/g (79). If granulated, the lowest energy level of the crystallized stage is not reached and the slag glass, richer in energy and potentially hydraulic, will fall to a lower energy level by forming, in the case of its reaction with water, hydration products with development of heat when alkaline or sulphate activators have been added (80).

Zachariasen (81) formulated a network theory of the structure of glass. The glass would consist of a three-dimensional net of oxides called network formers, characterized by small ionic radii and high ionic valencies. A typical network former is silicon which surrounded by oxygen atoms in a fourfold coordination, would form a tetrahedron in the form of SiO_4^{4-} tetrahedra, $Si_2O_7^{6-}$ or other groups from the sharing of oxygen atoms by two tetrahedra. The anionic groups would be neutralized by the positive valence of network modifiers such as Ca^{2+}, located in the cavities of the network. A low degree of polymerization of the tetrahedra would enhance the role of the network modifiers, generally of larger ionic radii and higher coordination number, resulting in a glass of smaller stability and higher hydraulic activity (82). Aluminum and magnesium in either fourfold or sixfold coordination can act as network formers or modifiers. Studies on blast furnace slags show that they can coexist in the same material with both coordination numbers (76).

Roiak and Chkolnik (83) discussed the role of the physico-chemical parameters of the glassy and the crystalline phase on the activity of blast furnace slags. According to these authors, the metallic cations which act either as network formers or as network modifiers occupy different positions in the glass network according to their coordination number. The difference in the arrangement of those cations should be an essential factor affecting the slag reactivity because the energy needed to break the metal-oxygen bond should depend on the position of the

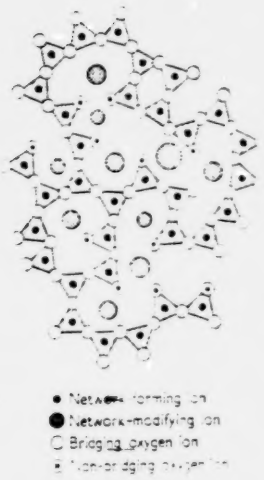

Fig. 11 - Schematic two-dimensional representation of glass according to the network theory (Ref. 81)

cation. The energy to break the metal-oxygen bond is a function of the dielectric constant of the media, which is water in the case of hydration, and of the energy of the ionic-covalent bond. When the latter decreases due to the dielectric constant of water and approaches the kinetic energy of the water molecules, the conditions are created for the passage into solution of the cations with a greater coordination number. Subsequently, to maintain the electrical neutrality of the system, cations with lower coordination number replace those cations transferred into the solution, affecting in turn the structure stability and bringing about the mobility of the $Si_xO_y^{2-}$ ions. The hydration process is enhanced by the increasing pH of the solution due to the presence of the hydrated cations, leading to the formation of the corresponding metal hydrosilicates. In this manner, the different nature of the interaction with water of crystalline and glassy materials of the same chemical composition could be explained in terms of changes in the structure of the mineral, produced by quenching.

Dron (84), in a statistical interpretation of Masson's (85) studies of ionic equilibria in liquid silicates, proposed a model whereby the Si atoms with one, two or three singly bonded oxygen atoms are distributed following a binomial law. The elements formed by the coordinated silica and oxygen atoms can constitute a simple ramification Y, a chain element E or an element of chain ending Z depending upon whether the number of coordinated oxygen atoms are three, two or one respectively (Fig. 7). Aluminum would appear in a chain crossing element in fourfold coordination with oxygen atoms. The presence of the group $(AlO_2)^-$ in the chain crossing element, susceptible to hydrolitic dissolution, would determine the slag reactivity (43,84).

Fierens et al. (86,87) proved the existence of superficial excited centers that would act as nuleation points in the formation of hydration products. The formation of structural defects constituting the activated centers is influenced by the rate on quenching. Recent studies (88) have shown that the hydraulic activity of granulated slags is mainly determined by the ratio of glass phase and microcrystalline phase and by the degree of polymerization of the glass phase, although when the degree of ionic bonds exceeds certain value, the degree of crystallization is likely to

increase. Another important factor related to hydraulic activity is the size and morphology of the microcrystalline phase. Air-cooled slags are less reactive and the degree of hydraulic activity varies with the mineral composition of the microcrystalline phase, decreasing in the following order: $C_2S > C_2AS > C_3S_2 > CS$.

Scarce information on the glass structure of non-ferrous slags is available at present. Baragano (59) reports that when heating a copper slag to 800°C in oxidizing atmosphere a partial destruction of the glass phase occurs, with formation of hematite and magnetite. When the temperature was raised to 1200°C, only cristobalite was found. Roper (60) studied the chemical composition of the glassy and the crystalline phases of a granulated copper reverberatory furnace slag as well as the composition of the cores and rims of zoned fayalite crystals. In the system SiO_2-Fe_2O_3-(CaO + MgO + Al_2O_3), similar to the composition of non-ferrous slags, the structure of these glasses has not been documented.

A considerable amount of empirical information has shown (57,58,89) that the pozzolanic activity of non-ferrous slags is related to their glass content. More efficient use of the slags pozzolanic activity could be made if a better understanding of their glass structure and of the hydration mechanism of non-ferrous slags could be achieved. As this particular area has not been fully explored, further work needs to be done in this direction.

EFFECT OF FINENESS ON THE KINETICS OF THE HYDRATION REACTIONS OF SLAGS AND SLAG BLENDS

The manufacture of slag cements that started in Germany towards the end of the 19th century was based in the intergrinding of granulated blast furnace slag with portland cement clinker.

Due to the problems posed by the variation in grindability, research was carried out in South Africa (90) directed to study development of slag cements. Separate grinding of slag showed to be technically advantageous, eliminating preferential grinding, improving storage conditions and making possible the optimization of the proportioning of slag and cement for concrete to meet mix specifications.

The empirical information available led some investigators to study the effect of fineness on the kinetics of slag cement hydration. Satarin

(91) observed that in slag cements the early mechanical resistance depends on the fineness of the clinker while the slag fineness contributes to the final resistance. Regourd (92) reported studies carried out on a slag cement composed of 85 wt per cent slag ground to approximately 5 700 cm/g, 13 wt per cent of portland cement clinker ground to 3 500 cm^2/g and 2 wt per cent gypsum. More ettringite was found in the slag cement mortar, by the reaction of gypsum with the C_3A of the clinker and the Al_2O_3 in the slag, than in the portland cement mortar. After 28 days of curing the size of the slag grains that had not yet reacted was between 10 and 20 µm. The higher flexure resistance of the specimens made with the finer slag was explained in terms of the crystallization of ettringite into fine fibers.

The effect of fineness of air-cooled and granulated Ni slags was investigated by Laneuville (58) as related to hydraulic index and strength development in mortars of portland cement-slag-lime binders. Free CaO as well as the fraction of SiO_2 and Al_2O_3 soluble in HCl were measured before and after the test. The increase of HCl soluble SiO_2 and Al_2O_3 pointed to the possibility of a pozzolanic reaction. X-ray diffraction analysis did not indicate the presence of C-S-H and therefore the mechanism of hydration could not be explained. Nevertheless, the effect of fineness in the kinetics of the hydration reactions was revealed by tests conducted on mortars.

CONCLUSIONS

It is assumed that the primary objective of any Canadian research project on the properties, nature and uses of slags as cementing materials, will be to maximize the use of slags as replacements for portland cement. This approach will have two benefits: (i) a reduction in the total energy consumed to manufacture cementing materials; (ii) a reduction in the quantities of industrial waste requiring disposal.

The information on hydration of cementitious materials summarized in this report leads to the following conclusions:

1) Although portland cement, iron blast furnace slags, pozzolans and non-ferrous slags such as copper, nickel or lead slags differ widely in chemical properties, the products of hydration in the presence of $Ca(OH)_2$ are very similar. In each case C-S-H is produced along with calcium

aluminate hydrates and $Ca(OH)_2$. When sulphate ions are present, alumino-sulphates are formed. The reactions are sustained by an adequate supply of CaO to the system. For portland cement this is available internally; slags and pozzolans require an external source.

2) The mechanism of the hydration processes of the non-ferrous slags in the presence of activators is not known. Virtually nothing is known on the performance of concretes incorporating non-ferrous slags other than those used for mine backfilling.

3) The morphology and the pore structure of pastes of non-ferrous slags in portland cement and lime mixes as well as the rate of strength development are largely determined by the reaction kinetics of the individual components. Such information is currently not available.

4) The content and physical characteristics of glass are the major factors influencing the hydraulicity of slags. These properties can be influenced by quenching conditions. An understanding of the effect of quenching, grinding and storage on the properties of vitreous slags is needed.

SUGGESTIONS FOR FURTHER STUDIES

Basic and applied research is needed to develop an understanding of the hydration reactions of all classes of slags.

Work in the fundamental research category is required in the following areas:

(a) The basic principles of hydraulic reactivity of quenched slags require examination with particular regard to the kinetics of reaction as they are influenced by the degree of molecular disorder and the surface characteristics of quenched materials.

(b) The nature of the phases formed during slag hydration and the ways in which paste and mortar properties are influenced by slag hydration require continuing study. In particular the differences in pore structure between portland cement pastes and pastes containing non-ferrous slags require clarification.

(c) The nature of the non-crystalline phases in both ferrous and non-ferrous slags require examination to provide basic background for the development of quality control tests.

The areas requiring applied research with regard to these materials are related to the optimization of quenching procedures, the measurement of reactivity and the development of quality control methods for ground slags and related materials.

The effects of non-ferrous slags in cement/slag systems have only been examined in a cursory way, largely with a limited application in view. Applied research on these materials is required to establish the limits to which their use as pozzolans can be extended into the structural concrete field and the degree to which their activity is influenced by quenching. Optimum quenching procedures require development as do test methods and studies of durability and performance. In essence, non-ferrous slags should be regarded as new materials and their full potential as cement supplements should be investigated. The following activities are suggested as a starting point for such investigations in Canada.

1. Non-ferrous slags from all potential Canadian sources should be examined and categorized to establish which are capable of exploitation as cement supplements. This study should include discussion with plant operators, examination of process procedures, sample collection and a detailed chemical, physical, mineralogical and pozzolanic assessment of the materials. Batches of the most promising materials should be vitrified on a laboratory or pilot-plant scale.

2. Any existing vitreous, non-ferrous slags presently available should be subjected to a preliminary evaluation in concretes in the laboratory and in the field. This study should include mix proportioning, strength development, durability and potential health and environmental hazards that might be associated with the use and handling of finely ground Cu, Ni or Pb slags. A field trial of slag cement backfill in an underground site would be valuable in providing back-up data for marketing non-ferrous slag-based cements in mining areas.

3. All available vitrification technologies should be surveyed with a view to establishing or developing an optimal procedure.

4. Methods of glass quality determination should be investigated and new procedures developed with the purpose of providing test methods for quality control of vitrified non-ferrous slags.

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